

Flux-Line Lattice Structures in Untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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A small angle neutron scattering study of the flux-line lattice in a large single crystal of untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is presented. In fields parallel to the c -axis, diffraction spots are observed corresponding to four orientations of a hexagonal lattice, distorted by the a - b anisotropy. A value for the anisotropy, the penetration depth ratio, of $\lambda_a/\lambda_b=1.18(2)$ was obtained. The high quality of the data is such that second order diffraction is observed, indicating a well ordered FLL. With the field at 33° to c a field dependent re-orientation of the lattice is observed around 3T.

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The remarkable properties of the mixed state in the cuprate high- T_c superconductors are of great current interest. In particular, the expectation that high- T_c superconductors have an unconventional pairing symmetry has led inevitably to the question: how does the structure of the flux-line lattice (FLL) differ between conventional and unconventional superconductors? The question has been taken up by several recent theoretical contributions [1–4] which predict a variety of interesting FLL effects all deviating from the benchmark triangular Abrikosov lattice. However, such discussions may presuppose that the crystallographic properties of the FLL are already well understood in the simplest low-field regime where unconventional effects are least prevalent. This has been far from the experimental truth. Observations require a probe sensitive to the microscopic arrangement of flux-lines. Direct imaging [5] and decoration techniques [6] all have inherent drawbacks, and muon spin rotation has not yet achieved the sophistication to resolve the most subtle effects [7]. By comparison, small angle neutron scattering (SANS) provides unrivalled insights into the crystallography of the FLL, and is the only technique capable of unequivocally resolving such questions.

The demanding nature of neutron experiments requires large single crystals (masses $\gtrsim 200\text{mg}$), and because of this $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) has been the cuprate of choice for SANS experiments [8]. However, the materials properties of YBCO are complicated. The presence of Cu-O chains which are aligned with the crystallographic b direction render the otherwise tetragonal structure orthorhombic. Upon cooling from the growth, twin boundaries form along $\{110\}$ directions separating domains of interchanged a and b axes. A strong interaction between flux-lines and these twin planes significantly influences FLL properties. There is a further effect of the chains. Although the orthorhombic distortion is only slight ($\approx 1\%$), the electronic structure is markedly affected, and the consequence is anisotropy within the ab -

plane of both superconducting [9,10] and normal state [11] properties. All previous SANS studies have been on heavily twinned crystals [12,13], and although observations of a pattern with four-fold symmetry were claimed to be due to unconventional $d_{x^2-y^2}$ pairing [12], it could not be discounted that alignment by twin planes, in combination with the a - b anisotropy, did not provide a more plausible explanation [14].

A new development in materials technology, involving the application of uniaxial stress during the cooling process, has made possible the growth of very large untwinned crystals [15]. In this paper we report SANS measurements on such untwinned single crystals of YBCO. The results show the effects of the a - b anisotropy on the FLL, and prove explicitly that the results from twinned crystals [12] cannot be interpreted as evidence for d -wave effects. Having clarified the low-field picture, we then present the first indication at higher fields that the range of validity of simple London scaling theory is limited.

The structure of the lattice formed by flux-lines in a superconductor is dictated in crude terms, as a function of flux-line density, by the intrinsic anisotropy of the electronic structure and the shape of the core of individual flux-lines, as well as by the extrinsic effects of flux-line pinning by defects and surfaces. The penetration depth, λ , and coherence length, ξ , being the parameters which define the two length scales of flux-line interactions, their ratio $\kappa = \lambda/\xi$ is naturally an important quantity. Where κ is not much bigger than unity, core interactions exist over the whole (H,T) space and structures ranging from triangular to square are observed, as in borocarbides [16] and Nb [17], as a manifestation of anisotropic electronic structures dependent upon the orientation of the applied field with respect to the atomic lattice. In high- κ superconductors, such as cuprates and low- T_c NbSe₂ [18], one would expect that core effects only become influential at fields comparable with H_{c2} , and at low enough fields a purely electrodynamic interaction model should

be sufficient. In a basic London model, incorporating anisotropy in the effective mass tensor, predictions for fields applied parallel to the principal c -axis are a hexagonal FLL which is degenerate in energy with respect to orientation with the atomic lattice [19]. In reality, the presence of even vanishingly small higher-order effects, intrinsic or extrinsic in origin, will be able to lift this degeneracy to produce a preferred orientation. Among intrinsic effects, it is in the structure of the vortex core that an unconventional pairing symmetry is revealed, calculations predicting it to be four-fold [2]. Free energy calculations have therefore been made incorporating four-fold symmetry through higher gradient terms in a GL-type theory [1,4], and in a complete microscopic derivation of non-local electrodynamics in a London model [3]. The predictions are for a distorted hexagonal lattice at low field transforming to a square lattice over a field range which is dependent upon adjustable parameters related to the strength of the $d_{x^2-y^2}$ contribution.

The measurements have been obtained over a series of experiments using three SANS instruments (D11, D17 and D22) at the Institut Laue-Langevin, Grenoble, France. A field was applied parallel to the incident neutron beam, and the FLL formed by cooling through T_c . Rotation of the sample about a vertical axis with respect to the field, and of the field and sample as one with respect to the beam were both possible. As in all static imaging techniques, we see the FLL structures "frozen in" at the irreversibility line near T_c . Two crystals were initially studied, of masses 312mg and 1125mg, grown and detwinned under the same conditions, and oxygenated in flowing O_2 at 490°C for optimal doping. Magnetization measurements showed T_c of 92K. Essentially identical results were obtained from both, and the work presented therefore relates solely to the larger.

In Figure 1, a diffraction pattern is shown, obtained at 1.5K with a relatively low field of 0.51T applied parallel to the c -axis. The diffraction spots lie in an elliptical ring, representing a FLL which is essentially polycrystalline. This is in distinct contrast to patterns obtained for twinned crystals [12,13] which show four-fold patterns. The ellipse shape is clearly due to the superconducting anisotropy between the a and b basal plane directions. For this to be observable requires that the bulk of the sample must have a single Cu-O chain orientation. For fields larger than B_{c1} [20], the axial ratio of the ellipse is equal to the ratio of the penetration depths, $\gamma_{ab} = \lambda_a/\lambda_b$ (making $\gamma^2 = m_a/m_b$ the effective mass ratio). The sign of the anisotropy is consistent with a reduced penetration depth λ_b due to the increased supercurrent flow along the chain direction. From fits to the ellipse of scattering, a value for γ of 1.18(2) was obtained. This is slightly higher than the 1.13 estimated by Bitter decoration [6], but in the lower range of values found by polarized reflectivity, $\gamma=1.3$ -1.6 [9], and Josephson tunnel junctions, $\gamma=1.2$ -1.7 [10]. That the variability is between samples rather than techniques is borne out by μ SR measurements on the same sample which give $\gamma=1.16$ (2) [21]. No field dependence in γ was observed.

Reflectivity measurements on strongly oxygen disordered samples give γ as low as 1.05 [22]. We conclude that the Cu-O chains in our crystal are slightly disrupted by a small concentration of oxygen vacancies or impurities.

The intensity distribution around the ring in Fig. 1, although unbroken, contains distinct diffraction spots. From the assessment of many such patterns, we conclude that four different flux-line lattice orientations are being observed, each contributing a hexagonal pattern of six spots distorted by the a - b anisotropy. The situation is illustrated in Fig 2. Two of the structures have a FLL plane oriented with the axes of the atomic lattice, and two have a plane at 45° to them (that is with the $\{110\}$ directions). Surprisingly, the latter two are the same as two of the four orientations observed in twinned crystals. The implication is that this crystal is not completely free of twins, although the domains of the opposite orientation must be a very small fraction of the volume otherwise a second set of spots aligned on an ellipse at right angles would be observed. A neutron study of the crystallography of these YBCO crystals has confirmed this [23], the minority orientation was found to be confined to less than 5% of the sample. The two 45° distorted hexagonal patterns correspond to part of the square pattern observed by Keimer *et al* [12], who claimed that the orientation and distortion were due to d-wave effects. It is made clear by the present observations that the FLL structures, instead, are controlled at these low fields by anisotropy plus twin plane pinning in the manner postulated earlier [14]. Although a non-local contribution to the penetration depth anisotropy is possible [24], the *field-dependence* of the flux lattice distortion argues against this being important.

By tilting the c -axis $\approx 1.5^\circ$ (about the vertical) away from the applied field direction the different nature of the FLLs is made apparent. As expected of flux-lines pinned along their length by extended defects, the two 45° FLLs remain fixed to the twin plane direction while the remaining two lie instead along the field direction. Consequently in Fig. 3, this remarkably clear pattern shows only the twelve first order spots of the lattices oriented with the a and b axes. A ring of second order reflections is testament that the FLL is well formed. The left-hand side is stronger because these spots have been brought closer to their Bragg condition by rotating the field and sample as one. The Bragg condition for spots of the 45° FLLs are separated a further 1.5° away, which is considerably larger than the rocking curve widths. Gaussians fits to individual spots gave full-widths at half-maximum of $0.65(5)^\circ$ and $0.71(5)^\circ$ for the a - b and 45° FLLs respectively (instrumental broadening contributes only 0.2°). These give a lower limit for the longitudinal correlation lengths of the flux-lines of $1.8\mu\text{m}$.

The intensity of a reflection integrated over its full rocking curve can be related to the penetration depth. The established expression for the structure factor derived from London theory [25] indicates that the intensity is proportional to λ^{-4} . Making this calculation for the rocking curve of the pattern in Fig. 3 requires that we

estimate the proportion of the total number of flux-lines contained in each lattice. The rocking curves give (within 10%) equal proportions of the intensity distributed between them. Using this, we obtain $\lambda=138(5)\text{nm}$. If we take $\lambda=\sqrt{\lambda_a\lambda_b}$, and use the already measured value of γ , $\lambda_a=150(6)\text{nm}$ and $\lambda_b=127(6)\text{nm}$ are obtained. The value of λ_a provides a useful check of the consistency of our results, as it is known to be insensitive to the state of the chain layers, and is therefore reproducible across samples. It is typically quoted as 155nm for optimal doping [26] which agrees within experimental error.

Over the range of fields investigated, up to a maximum of 4 Tesla, the FLL structure remained essentially unchanged. This may not be inconsistent with the various unconventional and non-local theories whose distortions, if present, may simply be too weak over this range. We note that the distorted square lattices observed by STM at higher fields [5] are not consistent with our observations. Our first indication of the breakdown of simple London scaling theory comes from measurements made with the field inclined at an angle to the c -axis.

Rotating the field away from c to large angles, another factor becomes important: the anisotropy between supercurrents along c compared with those in the ab -plane. Previous SANS measurements on twinned crystals have given $\gamma_c = \lambda_c/\lambda_{ab} \approx 4.5$ [13]. This γ_c anisotropy mixes with the γ_{ab} anisotropy. With b as the vertical axis of rotation the eccentricity of the ellipse is accentuated by γ_c adding to γ_{ab} , and at angles comparable to 30° from c a continuous highly eccentric ellipse of scattering is observed, indicating a polycrystalline FLL. In contrast, when a is the axis of rotation, spots from the two ab aligned FLLs remain, with the a -oriented FLL becoming dominant with increasing angle. This is the orientation expected from simple London theory [19]. A possible explanation for the difference rotating about the two axes, is that rotation about b leaves the chains perpendicular to the applied field, while rotation about a leads to a shallower angle between field and chain direction, suggesting an unexpected influence of the chain structure upon the flux-lines. At an angle of $\approx 33^\circ$ from c , shown in Fig. 4(a), the two anisotropies cancel, and an almost undistorted hexagonal pattern is observed, again with second order spots. The FLL is a -axis oriented; however, under the same conditions but at a field of 3.8T , the pattern in Fig. 4(b) is observed corresponding to a FLL oriented instead with the b -axis. There is clearly a field dependence to whatever mechanism is controlling the FLL orientation, or perhaps a crossover from the London mechanism at low flux-line density to another at high density. At present we have no explanation for the effect, and it may yet prove necessary to invoke core effects, perhaps of $d_{x^2-y^2}$ origin, to account for it.

In conclusion, we emphasise that the crystallography of the FLL must be considered in the context of a complicated variety of influences, before addressing the singular question of unconventional pairing. The results demonstrate the various implications for the FLL caused by the presence of CuO chains in YBCO; introducing mi-

crostructural complications of twinning, a basal plane anisotropy in the effective mass, and even the suggestion of an interaction between the flux-lines and the chain structure. To resolve whether the observed field dependant reorientation is an intrinsic feature of unconventional superconductivity will require experiments on cuprates free of chains and ideally with tetragonal symmetry.

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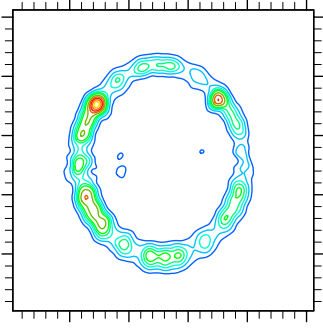


FIG. 1. The SANS pattern with 0.51T applied parallel to the c -axis; a -axis is vertical in the figure. The plot area covers 128×128 detector pixels, in reciprocal space $\pm 0.0173 \text{ \AA}^{-1}$; neutron wavelength $\lambda_n = 12 \text{ \AA}$, detector distance 14.5m, and collimation 14.4m.

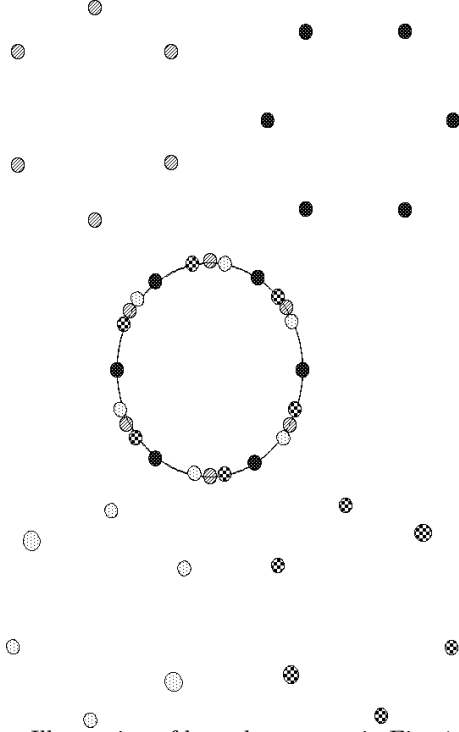


FIG. 2. Illustration of how the pattern in Fig. 1 is formed from two reciprocal lattices having planes oriented with the primary atomic lattices (top), and two having planes aligned with the $\{110\}$ and $\{1\bar{1}0\}$ twin planes (bottom) producing spots at 45° (emphasised).

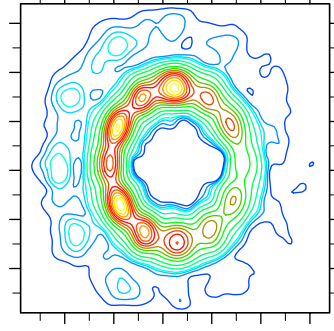


FIG. 3. The pattern with a field of 0.2T, not quite parallel to c . A ring of twelve first-order spots from two hexagonal lattices is visible, and remarkably well defined second-order spots. The plot covers 64×64 detector pixels, $\pm 0.0144 \text{ \AA}^{-1}$ in reciprocal space; $\lambda_n = 10 \text{ \AA}$, detector distance 14m, and collimation 13.6m.

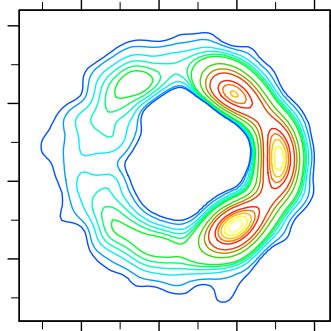
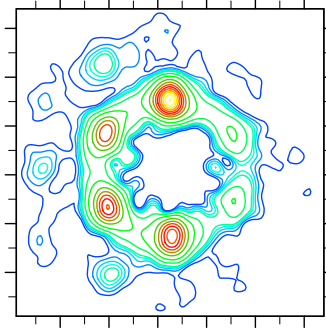


FIG. 4. The applied field tilted towards the b -axis at an angle of 33° to the c -axis. At 0.2T in the upper pattern a single hexagonal lattice aligned with the a -axis (vertical in the plots) is observed; $\pm 0.0144 \text{ \AA}^{-1}$, $\lambda_n = 10 \text{ \AA}$, detector distance 14m, and collimation 13.6m. At fields above 3T, the lower pattern changes to be oriented instead with the b -axis; $\pm 0.0503 \text{ \AA}^{-1}$, $\lambda_n = 10 \text{ \AA}$, detector distance and collimation are 2.5m.